

Synthesis and Microbial Studies of Binuclear Complexes of Nickel (II) and Cobalt(II)oxalatedihydrate with Rb- and Cs-salts of Oxygen and Nitrogen Containing Organic Acids

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ABSTRACT

A number of stable oxygen bridged heterobinuclear complexes of Nickel (II) and Cobalt(II)oxalatedihydrate with Rubidium and Cesium salts of Oxygen and Nitrogen containing organic acids such as 1N2N and 8HQ having general formulae $Ma(ox)_2H_2O.MbL$ have been synthesized, where $Ma=Ni/Co$, $OX = oxalate$, $Mb = Rb/Cs$, and $L = \text{deprotonated } 1N2N \text{ or } 8HQ$. These complexes were characterized by elemental analysis, UV- & IR-spectral analysis and magnetic moment measurement. These complexes were examined for their antimicrobial activity and found biologically active against *E.coli* and *C. albicans* and so these may be treated as good antibacterial agents and fungicides.

Keywords: 1N2N, 8HQ, antimicrobial studies, adduct, MIC.

1. INTRODUCTION

Like Schiff bases², oxalic acid, ethylenediamine and propylenediamine possess strong ability to form metal

complexes and they deserve proper attention because of their biological properties.

We describe here the preparation and characterization of heterobinuclear complexes of Ni(II) and Co(II)oxalatedihy-

hydrate with Rb- and Cs- metal complexes. The Nickel(II)oxalatedihydrate is green colored while Cobalt(II)oxalatedihydrate is grey colored powder, both are highly insoluble in water, have octahedral geometry⁵ and were obtained by mixing nickel sulfate and cobalt acetate with oxalic acid respectively in molar ratio 1:1 in aqueous medium. 8-Hydroxyquinoline (8HQ), also known as oxine, is an organic compound with the formula C_9H_7NO and monoprobidentate chelating agent. Its complexes exhibit antiseptic, disinfectant and pesticides⁴. 1-Nitroso-2-naphthol (1N2N) is also an organic compound with formula $C_{10}H_7NO_2$ and acts as an excellent chelating agent. It is the chelating ion exchanger in the synthesis of alumina adsorbents that are acidic, basic and neutral in nature. It is used for the removal and preconcentration of Pb(II), Cu(II) and Cr(II) from waste as well as drinking water. Rubidium and Cesium form stable complexes with 8-HQ and 1N2N¹. The bonding between metal oxalate and the Rubidium- and Cesium- salts is most likely to occur by dative bonding through oxygen atoms of carboxyl group of the ligand which has been supported by infrared spectra, electronic absorption spectra and magnetic measurement studies of the adducts. The minimum inhibitory concentration (MIC) of the prepared complexes Show the antimicrobial effectiveness.

2. EXPERIMENTAL

2.1 General

A.R grade reagents have been used for synthesizing all the compounds.

IR spectral results were recorded on a Perking-Elmer model 2000FT-IR

spectrophotometer from sophisticated analytical instrument facility, Central Drug Research Institute, Lucknow. UV-Visible spectral results were obtained in the Department of Chemistry, Patna University, Patna. It was recorded through SYSTRONICS Double Beam UV-VIS Spectrophotometer: 2210. Magnetic measurement data of complexes were obtained from Indian Instrumentation Centre, I.I.T, Roorkee. The adducts were tested for their antimicrobial activity against bacteria *Escherichia coli* and fungus *Candida albicans* by serial dilution method in DMF in the concentration range 25-100 $\mu g\ ml^{-1}$. Melting points were determined in open capillary tubes and are uncorrected. The purity of adducts were examined by TLC-using Silica gel-G, performing column chromatography.

2.2 Preparation of Rubidium and Cesium salts with 1N2N

Ethanol solution of 5.1g (0.05mole) RbOH and 8.1g(0.05 mole) of 1-nitroso-2-naphthol(1N2N) solution were slowly added in 25-35 ml of absolute ethanol. During addition, mixture was continuously stirred and then it was refluxed at 75-80°C for 2 hours, the dark green colored product was obtained, which was filtered, washed with absolute ethanol and then dried in an electric oven at 80°C.

Similar to above Cesium salt with 1N2N was prepared from alcoholic CsOH and 1N2N organic acid.

2.3 Preparation of Rubidium and Cesium salts with 8HQ

Ethanol solution of 5.1g (0.05mole) RbOH and 7.25g (0.05 mole) of

8-Hydroxyquinoline(8HQ) solution were slowly added in 25-35 ml of absolute ethanol. During addition, mixture was continuously stirred and then it was refluxed at 75-80°C for 2 hours, the pale-yellow product was obtained, which was filtered, washed with absolute ethanol and then dried in an electric oven at 80°C.

Similar to above Cesium salt with 8HQ was prepared from alcoholic CsOH and 8HQ organic acid.

2.4 Preparation of adducts $\text{Co}(\text{OX})_2\text{H}_2\text{O}$. $\text{M}_b\text{L}(\text{M}_b=\text{Rb or Cs, L}=1\text{N}2\text{N or 8-HQ})$

$\text{Co}(\text{OX})_2\text{H}_2\text{O}$ was taken in absolute ethanol in two conical flask and Rb/Cs salts of 1N2N in one conical flask while Rb/Cs-salts of 8-Hydroxyquinoline (8HQ) were added in other conical flask in the molar ratio of 1:1. They were refluxed with constant stirring on hot plate for 2 hours. Everything went into solution after half an hour and then the adducts were precipitated in hot condition. These were allowed to cool filtered, washed with absolute ethanol and dried in an air oven at 80°C.

2.5 Preparation of adducts $\text{Ni}(\text{OX})_2\text{H}_2\text{O}$. $\text{M}_b\text{L}(\text{M}_b=\text{Rb or Cs, L}=1\text{N}2\text{N or 8-HQ})$

$\text{Ni}(\text{OX})_2\text{H}_2\text{O}$ was taken in absolute ethanol in two conical flask and Rb/Cs salts of 1N2N in one conical flask while Rb/Cs-salts of 8-Hydroxyquinoline (8HQ) were added in other conical flask in the molar ratio of 1:1. They were refluxed with constant stirring on hot plate for 2 hours. Everything went into solution after half an hour and then the adducts were precipitated in hot condition. These were allowed to cool

filtered, washed with absolute ethanol and dried in an air oven at 80°C.

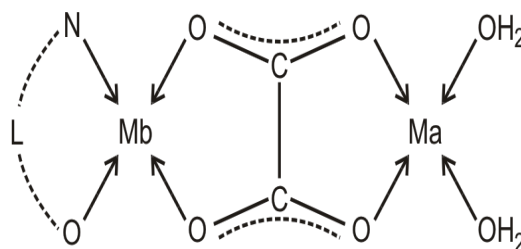
The physical properties of $\text{Ni}(\text{OX})_2\text{H}_2\text{O}$ and $\text{Co}(\text{OX})_2\text{H}_2\text{O}$ and their adducts formed with Rb&Cs-salts are shown in Table-i

3. RESULT AND DISCUSSION

3.1 Spectral studies and Magnetic moment measurement

The magnetic and electronic spectral studies reveal a break in the polymerized system of $\text{Ni}(\text{Ox})\cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{Ox})\cdot 2\text{H}_2\text{O}$. The polymeric octahedral Ni(II) and Co(II) ions are converted into tetrahedral ones, in the adducts.

The bonding between metal oxalate and the Rubidium and Cesium -salts are most likely through oxygen atoms of carboxyl group. This has been supported by IR spectral (showing bridging oxalate group), magnetic moments and electronic spectral studies show tetrahedral stereochemistry of adducts. Two water molecules are coordinated to the metal ion of the 'complex ligands'. The probable structure and bonding of the newly prepared adducts of the general formula $[\{\text{Ma}(\text{Ox})_2\text{H}_2\text{O}\}\text{MbL}]$ has been shown in the figure



Where, Ma = Ni(II) or Co(II); Mb = Rb or Cs.
L = deprotonated 8HQ or 1N2N

3.2 Antimicrobial activity

The prepared adducts were tested for their antimicrobial activity against bacteria *E. Coli* and fungus *Candida albicans* by serial dilution method in DMF in the concentration range 25-100 μ g /ml. Gentamycin, Ampicilin, Chloramphenicol,

Ciprofloxacin, Norfloxacin, Nystatin and Greseofulvin were used as standard for the examination of antibacterial and antifungal activities. The activity was reported by minimum inhibitory concentration(MIC)³. The MIC result of the prepared adducts are summarized in Table-2.

Table-1: Physical Properties of Metal chelates and their adducts formed with Rb/Cs-salts

Compounds	Color	Decoma. Temp(°C)	μ_{eff}	Elemental Analysis(%)			Yield (%)
				Co/Ni	Rb/Cs	N	
Ni(OX) ₂ H ₂ O	Green	295	3.40	-	-	-	85
Ni(OX)2H ₂ ORb1N2N	Greenish brown	310	3.57	13	3.12	19.10	81
Ni(OX)2H ₂ ORb8HQ	Pale brown	335	3.60	13.91	3.00	20.00	81
Ni(OX)2H ₂ OCs1N2N	Brown	312	3.52	11.85	2.76	21.06	84
Ni(OX)2H ₂ OCs8hq	Greenish yellow	340	3.58	12.40	2.85	28.10	83
Co(OX)2H ₂ O	Grey	290	5.20	-	-	-	81
Co(OX)2H ₂ ORb1N2N	Brownish yellow	305	5.10	13.80	3.75	19.25	83
Co(OX)2H ₂ Orb8HQ	Light yellow	310	5.15	13.90	3.20	20.00	82
Co(OX)2H ₂ OCs1N2N	Brickish red	312	5.00	12.00	2.80	27.00	80
Co(OX)2H ₂ OCs8HQ	Yellowish	315	5.18	12.30	2.90	28.00	80

Table-2: MIC values of prepared adducts

Compounds	concentration	Percentage inhibition	
		<i>E. Coli</i>	<i>C. albicans</i>
Ni(OX)2H ₂ ORb1N2N	100	100	100
	50	90-95	90-92
	25	40-50	40-50
Ni(OX)2H ₂ OCs8HQ	100	100	100
	50	90-95	85-90
	25	40-50	50-55
Co(OX)2H ₂ ORb1N2N	100	100	100
	50	90-95	90-95
	25	50-55	50-52
Co(OX)2H ₂ ORb8HQ	100	100	100
	50	90-94	92
	25	50-55	50-52
1. Co(OX)2H ₂ OCs1N2N	100	100	100
	50	90	92
	25	45-50	52-55

4. CONCLUSION

The interesting purpose of this research work was to synthesize, characterize and examine the antimicrobial activities of the adducts having General formulae $\text{Ma}(\text{OX})_2\text{H}_2\text{OMbL}$, where $\text{Ma}=\text{Ni}/\text{CO}$, $\text{Mb}=\text{Rb}/\text{Cs}$ and $\text{L}=\text{1N2N}$ or 8HQ . The structure of prepared adducts were confirmed with the help of IR-spectra, Electronic spectra and magnetic moment measurement. MIC^3 values revealed that most of the adducts of Ni(II) and Co(II) oxalate formed with Rb or Cs-salts of 1N2N & 8HQ show great degree of antimicrobial activity at high concentration against tested organism.

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UV-spectra and magnetic moment measurement respectively. Authors are also thankful to Lab of Biotechnology and Molecular Biology, Department of Botany B.N. College Patna for study of biological activities.

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